

(3) climatic warming, perhaps coeval to the termination of the Sun's T Tauri phase, and resulting poleward latitudinal shift of the zones of preserved ground ice.

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A CARBON DIOXIDE/METHANE GREENHOUSE ATMOSPHERE ON EARLY MARS. L. L. Brown and J. F. Kasting, Department of Geosciences, Pennsylvania State University, University Park PA 16802, USA.

One explanation for the formation of fluvial surface features on early Mars is that the global average surface temperature was maintained at or above the freezing point of water by the greenhouse warming of a dense CO₂ atmosphere [1]; however, Kasting [2] has shown that CO₂ alone is insufficient because the formation of CO₂ clouds reduces the magnitude of the greenhouse effect. It is possible that other gases, such as NH₃ and CH₄, were present in the early atmosphere of Mars and contributed to the greenhouse effect. Kasting et al. [4] investigated the effect of NH₃ in a CO₂ atmosphere and calculated that an NH₃ mixing ratio of $\sim 5 \times 10^{-4}$ by volume, combined with a CO₂ partial pressure of 4-5 bar, could generate a global average surface temperature of 273 K near 3.8 b.y. ago when the fluvial features are believed to have formed. Atmospheric NH₃ is photochemically converted to N₂ by ultraviolet radiation at wavelengths shortward of 230 nm; maintenance of sufficient NH₃ concentrations would therefore require a source of NH₃ to balance the photolytic destruction. We have used a one-dimensional photochemical model to estimate the magnitude of the NH₃ source required to maintain a given NH₃ concentration in a dense CO₂ atmosphere [5]. We calculate that an NH₃ mixing ratio of 10⁻⁴ requires a flux of NH₃ on the order of 10¹² molecules cm⁻² s⁻¹. This figure is several orders of magnitude greater than estimates of the NH₃ flux on early Mars; thus it appears that NH₃ mixed with CO₂ is not enough to keep early Mars warm.

We are currently using a one-dimensional radiative-convective climate model to determine the greenhouse effect of CH₄ in a CO₂ atmosphere. Atmospheric CH₄ would have a longer lifetime than NH₃ because CH₄ photolysis occurs only at wavelengths shortward of 145 nm, whereas NH₃ is photolyzed out to 230 nm. Hydrocarbon aerosols, which are formed as a product of CH₄ photolysis, are highly absorbent and may have provided a UV shield that would have lengthened the photochemical lifetime of CH₄ itself, as well as other hydrocarbon gases and NH₃. The greenhouse effect resulting from the combination of these gases and particles could conceivably have raised the mean global surface temperature of Mars to near the H₂O freezing point. A combination of radiative-convective climate modeling and photochemical modeling should show whether this idea is feasible and how large a CH₄ source would be needed.

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OXIDATION OF DISSOLVED IRON UNDER WARMER, WETTER CONDITIONS ON MARS: TRANSITIONS TO PRESENT-DAY ARID ENVIRONMENTS. R. G. Burns, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge MA 02139, USA.

Introduction: The copious deposits of ferric-iron assemblages littering the surface of bright regions of Mars indicate that efficient oxidative weathering reactions have taken place during the evolution of the planet. Because the kinetics of atmosphere-surface (gas-solid) reactions are considerably slower than chemical weathering reactions involving an aqueous medium, most of the oxidation products now present in the martian regolith probably formed when groundwater flowed near the surface. This paper examines how chemical weathering reactions were affected by climatic variations when warm, wet environments became arid on Mars. Analogies are drawn with hydrogeochemical and weathering environments on the Australian continent where present-day oxidation of iron is occurring in acidic groundwater under arid conditions.

Background: Chemical weathering reactions of basaltic rocks are facilitated in aqueous solutions. Several stages are involved [1-3], including (1) dissolution of basaltic glass, iron sulfides, and ferromagnesian silicate minerals, which deliver soluble Mg²⁺, Fe²⁺, Ca²⁺, silica, etc., to groundwater; (2) ferrololysis, during which oxidation of dissolved Fe²⁺ occurs, producing soluble Fe³⁺ ions, which are eventually hydrolyzed to Fe(III) oxyhydroxy- and hydroxysulfato gels and colloids; and (3) precipitation of poorly crystalline ferric oxides, oxyhydroxides, and sulphate minerals, as well as clay silicate and evaporite minerals, in depositional environments such as the martian regolith.

Rates of chemical weathering of Fe²⁺-bearing minerals in aqueous environments that are applicable to the martian surface have been estimated from experimental data for basaltic minerals [2,3]. Reaction rates are strongly influenced by acidity or pH [4,5], as well as salinity or ionic strength [6], concentration of dissolved O in aerated groundwater [7,8], and temperature [7,8]. In acidic groundwater (pH < 4.5), silicate minerals dissolve rapidly, but rates of oxidation of aqueous Fe²⁺ ions are very slow, particularly in brines at low temperatures.

For example, rates of dissolution of olivine and pyroxenes range from about 1400 ppm Fe m⁻² yr⁻¹ (pH 2 at 25°C) to 2 × 10⁻² ppm Fe m⁻² yr⁻¹ (pH 6 at 0°C). In acidic ice-cold saline solutions (pH 4.5 at 0°C), dissolution rates are about 1 ppm Fe m⁻² yr⁻¹. In such melt waters saturated with O in the present-day martian atmosphere (P_{O₂} = 10⁻⁵ bar), the rate of oxidation of dissolved Fe²⁺ is also about 1 ppm Fe m⁻² yr⁻¹. Rates of oxidation are much higher in near-neutral pH saline groundwater and brines; thus, for brines with ionic strengths of 1 to 5 molal, rates of oxidation range from 500 to 900 ppm Fe m⁻² yr⁻¹ (pH 6 at 0°C) to about 100 ppm Fe m⁻² yr⁻¹ (pH 6 at -25°C). Such relatively low rates of oxidation of aqueous Fe²⁺ contrast with the very high values for terrestrial river water ($\approx 1.8 \times 10^7$ ppm Fe m⁻² yr⁻¹ for pH 6 at 25°C), and for deep ocean bottom water ($\approx 5 \times 10^6$ ppm Fe m⁻² yr⁻¹ for pH 8.2 at 2°C). On Mars, the rate of oxidation of dissolved Fe²⁺ in aerated near-neutral pH saline solutions would exceed the rate of supply of dissolved Fe, except in very acidic groundwater.

Calculations indicate that the mixing ratio of O in the present-day martian atmosphere is not being regulated by the oxidation of